

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 06-248164
(43)Date of publication of application : 06.09.1994

(51)Int.Cl. C08L 65/00
C08J 5/18
C08J 5/24
C08K 5/02
C08K 5/10
C08K 5/14
C08K 5/3477
C08L 45/00

(21)Application number : 05-351125 (71)Applicant : NIPPON ZEON CO LTD
(22)Date of filing : 28.12.1993 (72)Inventor : KOUJIMA YUUJI
OBARA TEIJI
NATSUUME YOSHIO

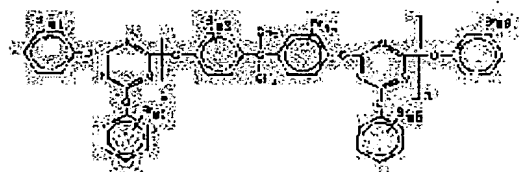
(30)Priority
Priority number : 04361131 Priority date : 28.12.1992 Priority country : JP

(54) CROSSLINKABLE NORBORNENE RESIN COMPOSITION AND MOLDING MADE THEREFROM

(57)Abstract:

PURPOSE: To obtain the subject composition which can give a molding improved in electrical insulation properties, heat resistance, chemical resistance, etc., by mixing a thermoplastic hydrogenated ring-opening norbornene resin with an organic peroxide, a crosslinking aid and a specified flame retardant.

CONSTITUTION: 100 pts.wt. thermoplastic hydrogenated ring-opening norbornene resin of a molecular weight of 10000-200000 and a degree of hydrogenation of 90% or above is melt-mixed with 0.001-30 pts.wt. organic peroxide, 0.1-10 pts.wt. wt., per pt.wt. organic peroxide, crosslinking aid and optionally 5-150 pts.wt. flame retardant of formula I or II (wherein (n) and m1 to M6 integers; $n \geq 0$; $1 \leq m1 \leq 5$; $1 \leq m2 \leq 5$; $1 \leq m3 \leq 4$; $1 \leq m4 \leq 5$; $1 \leq m5 \leq 5$; and $1 \leq m6 \leq 5$) to obtain a resin composition. This resin composition is molded and crosslinked at 80-350° C for 5-120 min to obtain a crosslinked molding having a water absorptivity of 0.03% or below, an insulation resistance of 10¹⁵ to 10¹⁷Ω, a dielectric constant of 2.0-2.5 at 1MHz and a dielectric loss tangent of 0.0001-0.0007.



LEGAL STATUS

[Date of request for examination] 27.12.2000
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number] 3319116

[Date of registration]

21.06.2002

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

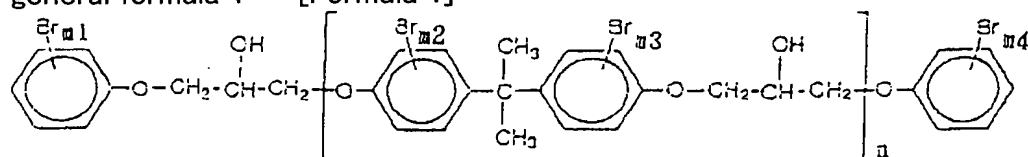
[Claim(s)]

[Claim 1] The uniform cross-linking norbornene system resin constituent which distributes the bridge formation assistant 0.1 – 10 weight sections, and changes to organic peroxide 0.001 – 30 weight sections, and the organic peroxide 1 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section.

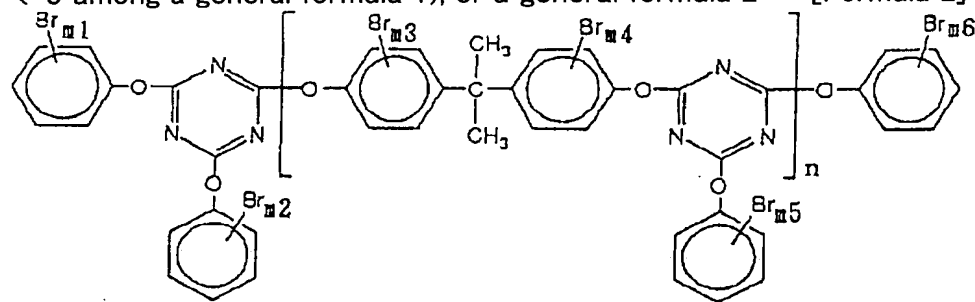
[Claim 2] The cross-linking norbornene system resin constituent according to claim 1 whose rate of hydrogenation of this hydrogenation ring breakage norbornene system resin is 90% or more.

[Claim 3] Claim 1 this whose bridge formation assistant is an allyl compound system bridge formation assistant or a methacrylate system bridge formation assistant, or a cross-linking norbornene system resin constituent given in two.

[Claim 4] the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section -- a general formula 1 -- [Formula 1]



(n, m1, m2, m3, and m4 being integers, and they being $n \geq 0$, $1 \leq m1 \leq 5$, $1 \leq m2 \leq 4$, $1 \leq m3 \leq 4$, and $1 \leq m4 \leq 5$ among a general formula 1), or a general formula 2 -- [Formula 2]



(n, m1, m2, m3, m4, m5, and m6 are integers among a general formula 2.) $n \geq 0$ and $1 \leq m1 \leq 5$, $1 \leq m2 \leq 5$, $1 \leq m3 \leq 4$, and $1 \leq m4 \leq 4$, $1 \leq m5 \leq 5$, and $1 \leq m6 \leq 5$ -- it is -- claims 1 and 2 which carry out 5-150 weight section addition of the flame retarder expressed, and change, or a cross-linking norbornene system resin constituent given in three.

[Claim 5] Claims 1, 2, and 3 or cross-linking mold goods which consists of a cross-linking norbornene system resin constituent given in four.

[Claim 6] A film or cross-linking mold goods according to claim 5 which is sheets.

[Claim 7] Cross-linking mold goods according to claim 5 which are prepreg.

[Claim 8] Claims 5 and 6 or bridge formation mold goods over which heat cross-linking mold goods given in seven, and they are made to construct a bridge.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the cross-linking norbornene system resin constituent excellent in electric insulation, the cross-linking mold goods which change, and bridge formation mold goods.

[0002]

[Description of the Prior Art] With the advance of a technique, the demand of improvement in the speed of data processing, a raise in reliance, densification, etc., etc. increases, and, as for circuits, such as precision mechanical equipments, such as a computer and a transmitter, high performance-ization, such as multilayering of the circuit board, highly-precise-izing, and detailed-izing, is progressing.

[0003] Conventionally, as such the circuit board, phenol resin, an epoxy resin, polyimide resin, the fluororesin, or the polybutadiene resin is used, and it is improved according to an advance of a technique (JP,60-84317,A, JP,60-258233,A, JP,60-202130,A, JP,3-37256,A, JP,3-55237,A, JP,3-166256,A, JP,3-275760,A, etc.).

[0004] However, when difficulty was usually in an electrical property since 4.0 or more and a dielectric dissipation factor have the dielectric constant as high as 0.01 or more, and these resin was used for the circuit board etc., improvement in the speed of data processing and a raise in reliance were difficult for thermosetting resin, such as phenol resin, an epoxy resin, and polyimide resin. On the other hand, since the laminate of prepreg using thermoplastics, such as a fluororesin and a polybutadiene resin, was inferior to thermal resistance, a crack and exfoliation might arise, the dimensional stability of the laminate was also bad on the occasion of pewter attachment etc., and it was difficult [to multilayer] for it.

[0005] The method of improving thermal resistance, solvent resistance, etc. is proposed from carrying out organic peroxide bridge formation of the thermoplastic norbornene system resin recently. For example, by the approach indicated by JP,62-34924,A, after grinding after kneading resin and a bridge formation assistant, infiltrating an organic peroxide solution into it and removing a solvent, the approach of carrying out press forming and constructing a bridge is indicated. However, in such a procedure, a process is complicated and there is a problem that organic peroxide does not necessarily distribute to homogeneity, the top where effectiveness is bad. Moreover, the thermoplastic norbornene system resin currently indicated in this official report was a norbornene system monomer and the copolymer of ethylene, when it was going to construct the bridge with organic peroxide by this approach, the fall of the molecular weight by disassembly of a polymer often produced the hydrogenation ring breakage norbornene system resin which is not indicated, and it became clear that thermal resistance required for pewter attachment etc. was not obtained.

[0006] Moreover, in JP,2-255848,A, it is hydrogenation ring breakage norbornene system resin. Although constructing a bridge using organic peroxide in the resin constituent which blended amorphism nature or the alpha olefin system copolymer of low crystallinity and amorphism nature, or the styrene system copolymer of low crystallinity with the included thermoplastic norbornene system resin is indicated, there is no example over which the bridge was concretely constructed about hydrogenation ring breakage norbornene system resin, and constructing a bridge using organic peroxide in the hydrogenation ring breakage norbornene system resin which does not blend these special resin is not indicated. Furthermore, in this official report, organic peroxide, a bridge formation assistant, and a flame retarder are blended with such a resin constituent. Although the approach of blending a flame retarder is indicated after blending the approach, resin, and organic peroxide which construct a bridge and constructing a bridge By the approach of blending a flame retarder after bridge formation, when using for the laminate of prepreg etc., it is hard to distribute a flame retarder to homogeneity. When there is a problem of not being practical, and a flame retarder is blended before bridge formation and only hydrogenation ring breakage norbornene system resin is used as resin In the flame retarder illustrated by this official report, there was a problem from which it denaturalizes with organic peroxide and sufficient fire retardancy is not acquired that there were some which are not distributed to homogeneity.

[0007]

[Problem(s) to be Solved by the Invention] Then, this invention persons were excellent in thermal resistance, find out that a bridge can be constructed without producing disassembly of a polymerization band if thermoplastic hydrogenation ring breakage norbornene system resin is made to distribute organic peroxide and a bridge formation place agent to homogeneity as a result of wholeheartedly research for the purpose of development of the mold goods which consist of a dielectric constant and the low resin of a dielectric dissipation factor, and came to complete this invention.

[0008]

[Means for Solving the Problem] In this way, according to this invention, the cross-linking mold goods which consist of the uniform cross-linking norbornene system resin constituent and this cross-linking norbornene system resin constituent which distribute the bridge formation assistant 0.1 – 10 weight sections, and change to organic peroxide 0.001 – 30 weight sections, and the organic peroxide 1 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section, and the bridge formation mold goods over which heat these cross-linking mold goods and they are made to construct a bridge are offered.

[0009] (Thermoplastic hydrogenation ring breakage norbornene system resin) In JP,3-14882,A, JP,3-122137,A, etc., the thermoplastic hydrogenation ring breakage norbornene system resin used for this invention is well-known resin, and, specifically, is the hydrogenation object of the ring-opening-polymerization object of a norbornene system monomer.

[0010] A norbornene system monomer is also a monomer well-known at the above-mentioned official report, JP,2-227424,A, JP,2-276842,A, etc. For example, norbornene, its alkyl, alkylidene, an aromatic substitution derivative and these permutations, or the halogen of an unsubstituted olefin, A hydroxyl group, an ester group, an alkoxy group, a cyano group, an amide group, an imide radical, Polar-group substitution products, for example, 2-norbornene, such as a silyl radical, 5-methyl-2-norbornene, 5 and 5-dimethyl-2-norbornene, 5-ethyl-2-norbornene, 5-butyl-2-norbornene, 5-ethylidene-2-norbornene, 5-methoxycarbonyl-2-norbornene, 5-cyano-2-norbornene, 5-methyl-5-methoxycarbonyl-2-norbornene, 5-phenyl-2-norbornene, 5-phenyl-5-methyl-2-norbornene, 5-hexyl-2-norbornene, 5-octyl-2-norbornene, 5-octadecyl-2-norbornene, etc.; The monomer which one or more cyclopentadienes added to norbornene, The same derivative and same substitution product as the above, 1 [for example,], 4:5, 8-dimethano – 1, 2, 3, 4, 4a, 5, 8, 8a-2, 3-cyclopentadieno naphthalene, The 6-methyl –1, 4:5, 8-dimethano – 1, 4,a [4], 5, 6, 7, 8, and 8a-octahydronaphthalene, 1, 4:5, 10:6, 9-trimethano – 1, 2, 3, 4,a [4], 5,a [5], 6, 9,a [9], 10, and 10a-dodeca hydronalium –2, 3-cyclopentadieno anthracene, etc.; A monomer, the same derivative and same substitution product as the above of the polycyclic structure which is the polymer of a cyclopentadiene, For example, a dicyclopentadiene, 2, a 3-dihydrodicyclopentadiene, etc.; The addition product of a cyclopentadiene, a tetrahydro indene, etc., The same derivative and same substitution product as the above, 1 [for example,], 4-methano – 1, 4, 4a, 4b, 5, 8, 8a, a 9a-octahydro fluorene, 5, the 8-methano –1, 2, 3, 4, 4a, 5 and 8, 8a-octahydro –2, 3-cyclopentadieno naphthalene, etc.; etc. -- it is mentioned.

[0011] A well-known approach may be used for the ring opening polymerization of a norbornene system monomer, and it may be copolymerized with the monomer in which other copolymerization is possible if needed. By the well-known approach, a polymer may be denatured using an organic silicon compound and a partial saturation epoxy monomer with the radical in which alpha and beta-unsaturated carboxylic acid and/or its derivative, a styrene system hydrocarbon, an olefin system unsaturated bond, and hydrolysis are possible by JP,3-95235,A etc. It considers as thermoplastic hydrogenation ring breakage norbornene system resin by hydrogenating these resin. You may denaturalize resin after hydrogenation.

[0012] GPC (gel purge ESHON chromatography) to which the molecular weight of hydrogenation ring breakage norbornene system resin uses a cyclohexane as a solvent -- the polystyrene reduced property measured by law -- it is -- 10,000-200,000 -- desirable -- 20,000-100,000 -- it is 25,000-50,000 more preferably. When number average molecular weight is too small, a mechanical strength is inferior, and if too large, a moldability will worsen. Moreover, the rate of hydrogenation is 99% or more more preferably 95% or more 90% or more in order to raise heat-resistant degradation nature and photodegradation-proof nature.

[0013] as long as it can distribute at homogeneity to the hydrogenation ring breakage norbornene system resin used by this invention -- a request -- antioxidants, such as a phenol system and the Lynn system; Heat deterioration inhibitors, such as a phenol system; UV stabilizer, such as a benzophenone system; Antistatic agents, such as an amine system; Lubricant, such as ester of fatty alcohol, partial ester of polyhydric alcohol, and the partial ether; etc. -- various additives may be added.

[0014] (Organic peroxide) The organic peroxide used for this invention It is not limited especially but is easy to be well-known at JP,62-34924,A etc. For example, t-butyl hydroperoxide, p-menthonaphtene hydroperoxide, Hydroperoxide, such as cumene hydroperoxide; JIKUMIN peroxide, Dialkyl peroxide, such as t-butyl cumin peroxide, alpha, and alpha'-screw (tert-butyl peroxide-m-isopropyl) benzene; Dipropionyl peroxide, Diacyl

peroxide, such as benzoyl peroxide; 2, 5-dimethyl -2, 5-di-tert-butyl peroxide; hexane, 2, the 5-dimethyl -2, 5-di-tert-butyl peroxide hexyne - Peroxy ketals, such as 3, 1, and 3-JI (t-butyl PAKI seesaw propyl) benzene; T-butyl peroxyacetate, peroxy ester, such as t-butyl peroxybenzoate; Ketone peroxide, such as peroxy cull BONATO, such as tert-butyl peroxide isopropyl cull BONATO and JI (isopropyl peroxy) dicarbonate; etc. -- it is mentioned.

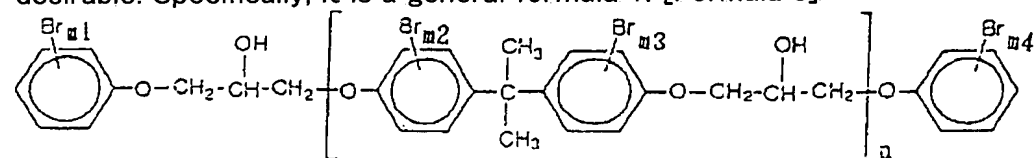
[0015] The bridge formation assistant used for this invention is not limited especially, either, but it is easy to be well-known [an assistant] at JP,62-34924,A etc. (Bridge formation assistant) Oxime nitroso ***** assistants, such as quinonedioxime, benzoquinone dioxime, and p-nitrosophenol; Maleimide system bridge formation assistants, such as N and N-m-phenylene bismaleimide; Diallyl phthalate, Allyl compound system bridge formation assistants, such as a triaryl SHIANU rate and triallyl isocyanurate; Ethylene glycol dimethacrylate, methacrylate system bridge formation assistants, such as trimethylolpropanetrimethacrylate; Vinyl system bridge formation assistants, such as vinyltoluene, ethyl vinylbenzene, and a divinylbenzene; etc. -- it is illustrated. Especially, an allyl compound system bridge formation assistant and a methacrylate system bridge formation assistant are easy to distribute homogeneity, and desirable.

[0016] (Cross-linking norbornene system resin constituent) The cross-linking norbornene system resin constituent of this invention is a uniform constituent which adds organic peroxide and a bridge formation assistant to thermoplastic hydrogenation ring breakage norbornene system resin, and grows into it.

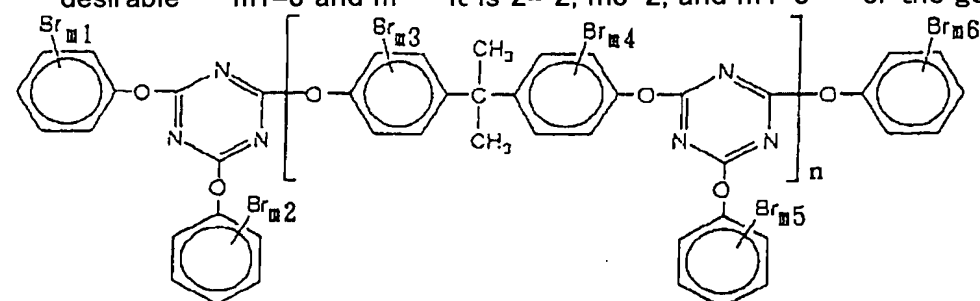
[0017] If there are too few additions of organic peroxide, since bridge formation will stop being able to happen easily, the organic peroxide more than 1 weight section is preferably added especially more than the 0.05 weight section more than the 0.01 weight section more than the 0.001 weight section to the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section. since [moreover,] the electrical property of the resin which constructed the bridge when there were too many additions of organic peroxide, a water resisting property, moisture resistance, etc. fall -- the thermoplastic hydrogenation ring breakage norbornene system resin 100 weight section -- receiving -- 30 weight sections -- desirable -- 15 weight sections -- more -- desirable -- 10 weight sections -- organic peroxide is added so that 5 weight sections may not be exceeded especially preferably.

[0018] moreover, the addition of a bridge formation assistant -- the organic peroxide 1 weight section -- receiving -- 0.1 - 10 weight section -- it is 0.2 - 5 weight section preferably. Since bridge formation cannot take place easily, hydrogenation ring breakage norbornene system resin will decompose and molecular weight will fall if there are too few additions of a bridge formation assistant, thermal resistance required for pewter attachment is not obtained. Since the electrical property of the resin which constructed the bridge when there were too many additions of a bridge formation assistant, a water resisting property, moisture resistance, etc. fall, it is not desirable.

[0019] Furthermore, in order to raise the fire retardancy of the bridge formation mold goods of this invention, it is desirable to make the norbornene system resin constituent of this invention distribute a flame retarder to homogeneity. As for the flame retarder used in this invention, what homogeneity can be distributed as a resin constituent, sets at the condition of having blended as a resin constituent and, and the process of crosslinking reaction, and does not denaturalize [does not decompose and] and deteriorate with organic peroxide is desirable. Specifically, it is a general formula 1. [Formula 3]



(n, m1, m2, m3, and m4 are integers among a general formula 1.) $n \geq 0$, $1 \leq m1 \leq 5$, and $1 \leq m2 \leq 4$, $1 \leq m3 \leq 4$, and $1 \leq m4 \leq 5$ -- desirable -- $2 \leq m1 \leq 4$ and $2 \leq m2 \leq 3$, $2 \leq m3 \leq 3$, and $2 \leq m4 \leq 4$ -- especially -- desirable -- $m1=3$ and $m2=2$, $m3=2$, and $m4=3$ -- or the general formula 2 [Formula 4]



($n, m_1, m_2, m_3, m_4, m_5$, and m_6 are integers among a general formula 2.) $n \geq 0$ and $1 \leq m \rightarrow 1 \leq m_1 \leq 5, 1 \leq m_2 \leq 5, 1 \leq m_3 \leq 4$, and $1 \leq m \rightarrow 4 \leq 4, 1 \leq m_5 \leq 5$, and $1 \leq m_6 \leq 5 \rightarrow 2 \leq m_1$ preferably $\leq 4, 2 \leq m_2 \leq 4, 2 \leq m_3 \leq 3$, and $2 \leq m \rightarrow 4 \leq 3, 2 \leq m_5 \leq 4$, and $2 \leq m_6 \leq 4 \rightarrow$ especially -- desirable -- $m \rightarrow 1 = 3, m_2 = 3, m_3 = 2$, and $m \rightarrow 4 = 2, m_5 = 3$, and $m_6 = 3 \rightarrow$ it is -- the flame retarder expressed can distribute to homogeneity, and it does not decompose, denaturalize and deteriorate with organic peroxide. an addition -- the hydrogenation ring breakage norbornene system resin 100 weight section -- receiving -- the 5 - 150 weight section -- desirable -- the 20 - 140 weight section -- it is the 40 - 120 weight section especially preferably.

[0020] Especially the approach of distributing a flame retarder at homogeneity organic peroxide, a bridge formation assistant, and if needed to hydrogenation ring breakage norbornene system resin has the approach of it not being limited, for example, making it mixing and distributing in a ring breakage resin solution, and removing a solvent, the approach of mixing and distributing, after ring breakage resin has fused, etc. Especially if the solvent of ring breakage resin also dissolves ring breakage resin, it will not be limited, for example, toluene, a xylene, ethylbenzene, a chlorobenzene, etc. can be used. In addition, in the approach of making carry out melting of the ring breakage resin, and mixing and distributing organic peroxide etc., it is the temperature which does not construct a bridge, and melting, mixing, and distribution must be able to be performed and this approach cannot be used depending on the combination of ring breakage resin, organic peroxide, and a bridge formation assistant. When heating in order to remove a solvent also in the approach of mixing and distributing in a ring breakage resin solution, it is necessary to carry out a temperature setup so that bridge formation may not take place.

[0021] (Cross-linking mold goods) In this invention, after fabricating a cross-linking norbornene system resin constituent, a bridge is made to construct and cross-linking mold goods are obtained.

[0022] The temperature which dissolves in a solvent, and fabricates or does not construct a bridge, or a bridge formation rate fuses and fabricates the approach of fabricating a cross-linking norbornene system resin constituent at temperature late enough so that aggravation of a moldability may not take place according to bridge formation in the middle of shaping. As a solvent, the solvent which dissolves the above-mentioned hydrogenation ring breakage norbornene system resin is used. Generally it dissolves in a solvent and fabricates.

[0023] The cross-linking norbornene system resin constituent which dissolved in the solvent is specifically cast, a solvent is removed, and it fabricates on a sheet or a film, or base materials, such as letter base materials of a cross, such as glass fabrics, an aramid cross, a polyester cross, and a nylon cross, the same mat-like base material of the quality of the material as these, a nonwoven fabric, kraft paper, and linter paper, are infiltrated, and it fabricates. Prepreg is illustrated as cross-linking mold goods which infiltrated the resin constituent into the base material.

[0024] (Bridge formation) In this invention, are independent or carry out a laminating, and heat cross-linking mold goods more than constant temperature, they are made to construct a bridge, and bridge formation mold goods are obtained. Although the temperature which produces crosslinking reaction is decided mainly with the combination of organic peroxide and a bridge formation assistant, generally it constructs a bridge 120 degrees C - 300 degrees C preferably 80-350 degrees C by heating in temperature of 150-250 degrees C still more preferably. Moreover, generally [it is desirable to make it about 4 times of the half-life of organic peroxide, and] bridge formation time amount is 20 - 60 minutes still more preferably preferably for 10 to 90 minutes for 5 to 120 minutes. When carrying out the laminating of the cross-linking mold goods and constructing a bridge, heat welding and bridge formation take place between each class, and the bridge formation mold goods of one are obtained.

[0025] (Bridge formation mold goods) As bridge formation mold goods of this invention, a laminate, the circuit board, an interlayer insulation film, the film for damp-proof-course shaping, etc. are illustrated as a thing made to construct a bridge.

[0026] For 0.03% or less and insulation resistance, the dielectric constant in 1015-1017ohm, and 1MHz and a dielectric dissipation factor are [water absorption] 2.0-2.5, and 0.0001-0.0007, respectively, and the bridge formation mold goods of this invention are usually excellent in the water resisting property and the electrical property compared with the conventional thermosetting resin production type article. On the other hand, thermal resistance is equivalent to the conventional thermosetting resin production type article, and even if it contacts a 260-degree C pewter to the laminate which carried out the laminating of the copper foil for 30 seconds, the above, such as exfoliation of copper foil and generating of blistering, is not accepted. The laminate which is the bridge formation mold goods of these things to this invention is desirable also as the circuit board.

[0027] Moreover, the bridge formation mold goods of this invention have the thing excellent in fire retardancy, and the desirable thing which specifically shows the fire retardancy which was superior to V-2 or it in UL-94 specification, what shows the fire retardancy of V-1 or V-0 is more desirable, and especially its thing that shows the fire retardancy of V-0 is desirable. What is necessary is just to use the cross-linking norbornene system

resin constituent containing the above-mentioned retarders, in order to obtain such cross-linking mold goods.

[0028] (Prepreg) In the prepreg which is one of the examples of the cross-linking mold goods of this invention, especially the base material is not limited but, generally can use letter base materials of a cross, such as glass fabrics used as prepreg and a substrate, an aramid cross, a polyester cross, and a nylon cross, the same mat-like base material of the quality of the material as these, a nonwoven fabric, kraft paper, linter paper, etc.

[0029] After manufacture of the prepreg using the cross-linking norbornene system resin constituent of this invention makes about 5 - 50 % of the weight of concentration dissolve a cross-linking norbornene system resin constituent into solvents, such as toluene, a cyclohexane, and a xylene, and infiltrates a base material into the solution that what is necessary is just to follow a conventional method, it is made to dry and it should just remove a solvent. As for prepreg, generally, it is desirable to make it become the thickness of about 50-500 micrometers.

[0030] (Sheet) Especially the method of manufacturing the sheet which is one of the examples of the cross-linking mold goods of this invention is not limited. Generally the casting method is used. For example, in solvents, such as toluene, a xylene, and a cyclohexane, it dissolves and the cross-linking norbornene system resin constituent of this invention is distributed so that it may become about 5 - 50 % of the weight of concentration, and it casts or applies on a smooth side, desiccation etc. removes a solvent, it exfoliates from a smooth side, and a sheet is obtained. What is necessary is it being desirable choosing an approach's twisting foaming by rapid desiccation, when desiccation removes a solvent's, for example, raising temperature and making it just fully volatilize a solvent, after volatilizing the extent solvent which is low temperature. What is necessary is just to use a metal plate, a carrier film made of resin, etc. which carried out mirror plane processing as a smooth side. When using the carrier film made of resin, the solvent which it is careful of and is used for the solvent resistance of the material of a carrier film and thermal resistance, and desiccation conditions must be decided. Generally the sheet obtained by the casting method has the thickness of 10 micrometers - about 1mm. these sheets construct a bridge -- an interlayer insulation film and a damp proof course -- a characteristic -- it can use as a ** film etc. Moreover, it can also use for manufacture of the laminate indicated below.

[0031] (Laminate) The laminate which is one of the examples of the bridge formation mold goods of this invention accumulates the above-mentioned prepreg and/or the sheet non-constructed a bridge, carries out heating compression molding, and is made into required thickness by carrying out bridge formation and heat welding. In using a laminate as the circuit board, the laminating of the conductive layer for wiring which consists of a metallic foil etc. is carried out, or it forms a circuit by surface etching processing etc. It not only carries out a laminating to the outer surface of the laminate which is a finished product, but the laminating of the conductive layer for wiring may be carried out to the interior of a laminate by the purpose etc. For the curvature prevention at the time of fabricating, such as etching processing, it is desirable to combine and to carry out a laminating to the candidate for vertical. For example, beyond the temperature according to the cross-linking norbornene system resin using the front face of the piled-up prepreg and/or the piled-up sheet that carries out heat weld, it usually heats at about 150-300 degrees C, about two 30 - 80 kgf/cm is pressurized, bridge formation and heat welding are carried out between each class, and a laminate is obtained.

[0032]

[Example] An example and the example of a comparison are raised to below, and this invention is explained still more concretely. In addition, insulation resistance, a dielectric constant, a dielectric dissipation factor, and water absorption are JIS. C It measured by 6481 and the following approaches estimated fire retardancy according to UL-94 specification.

[0033] Using a test piece with a thickness of 1/16 inch, the upper limit of a test piece is stopped by the clamp, a test piece is fixed perpendicularly, and the place of 12 inches is covered with cotton under a test piece. The fire of a gas burner is applied to the lower limit of a test piece for 10 seconds, the 1st burn time of a test piece is measured, if fire goes out, the fire of a gas burner will be again applied to a lower limit for 10 seconds, and the 2nd burn time of a test piece is measured. When setting total of ten data of the 1st burn time and the 2nd burn time to T about five test pieces and setting the greatest data to M, it was judged as V-0, V-1, V-2, and a rejection by the following criteria.

V-0: The melt which T did not blaze up to the clamp 10 or less seconds, and flame attached [50 or less seconds and M] falls, and cotton is not lit.

V-1: The melt which T did not blaze up to the clamp 30 or less seconds, and flame attached [250 or less seconds and M] falls, and cotton is not lit.

V-2: The melt which flame attached [250 or less seconds and M] although T did not blaze up to the clamp 30 or less seconds fell, and cotton was lit.

Rejection: Don't satisfy the requirements of above V-0, V-1, and V-2.

[0034] When the example 1 hydrogenation ring breakage norbornene system resin (ZEONEX 280, Nippon Zeon

Co., Ltd. make, glass-transition-temperature [of 140 degrees C], number-average molecular-weight 28,000 [about], 99.7% or more of rates of hydrogenation) 20 weight section, the alpha and alpha'-screw (tert-butyl peroxide-m-isopropyl) benzene 1 weight section, and the diallyl phthalate 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

[0035] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to the cross-linking norbornene system resin constituent solution obtained in the example 2 example 1 using the coater. It was left at 120 more degrees C for 10 minutes, and was made to dry for 20 minutes at 60 degrees C. Then, the formed sheet was removed from the SUS plate. The thickness of the obtained sheet was about 150 micrometers.

[0036] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm² might make 1mm in thickness.

[0037] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 4x10¹⁶ ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 2.4 and 0.0005 0.01% or less, respectively.

[0038] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours.

[0039] Moreover, the laminating of the 13 sheets was carried out, it pressed for 20 minutes, and heat welding was carried out and the test piece for fire-resistant sex test was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm² might make 1/16 inch in thickness. When fire retardancy was evaluated using this test piece, in UL-94 specification, it was a rejection.

[0040] In the cross-linking norbornene system resin constituent solution obtained in the example 3 example 1, it was immersed and the glass KURORU base material with a thickness of 0.1mm was taken out. After drying the glass-fabrics base material into which the cross-linking norbornene system resin constituent was infiltrated at 60 degrees C for 20 minutes, it was left for 10 minutes at 150 degrees C, and eight prepregs were obtained. 40% of the weight of this prepreg was the cross-linking mold goods of this invention, and thickness was about 110 micrometers.

[0041] The laminating of these eight prepregs was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm² might make 1mm in thickness.

[0042] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 1x10¹⁷ ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 2.7 and 0.0009 0.01%, respectively.

[0043] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94 specification, it was a rejection.

[0044] When the example 4 hydrogenation ring breakage norbornene system resin (ZEONEX 280) 20 weight section, the JIKUMIRU peroxide 1 weight section, and the trimethylolpropanetrimethacrylate 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

[0045] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to the cross-linking norbornene system resin constituent solution obtained in the example 5 example 4 using the coater. It was left at 120 more degrees C for 10 minutes, and was made to dry for 20 minutes at 60 degrees C. Then, the formed sheet was removed from the SUS plate. The thickness of the obtained sheet was about 150 micrometers.

[0046] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm² might make 1mm in thickness.

[0047] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 2x10¹⁶ ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 2.6 and 0.0007 0.02%, respectively.

[0048] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94

specification, it was a rejection.

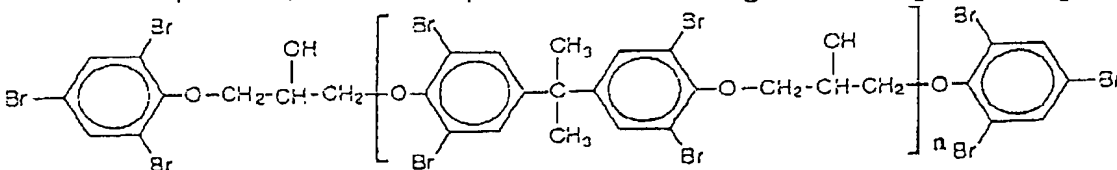
[0049] In the cross-linking norbornene system resin constituent solution obtained in the example 6 example 5, it was immersed and the glass KURORU base material with a thickness of 0.1mm was taken out. After drying the glass-fabrics base material into which the cross-linking norbornene system resin constituent was infiltrated at 60 degrees C for 20 minutes, it was left for 10 minutes at 150 degrees C, and eight prepregs were obtained. 40% of the weight of this prepreg was the cross-linking mold goods of this invention, and thickness was about 110 micrometers.

[0050] The laminating of these eight prepregs was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm2 might make 1mm in thickness.

[0051] Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 1×10^{17} ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 2.8 and 0.0011 0.03%, respectively.

[0052] The dissolution was not accepted, although swelling was accepted when it was immersed in toluene and this laminate was left for 24 hours. Moreover, when fire retardancy was evaluated like the example 2, in UL-94 specification, it was a rejection.

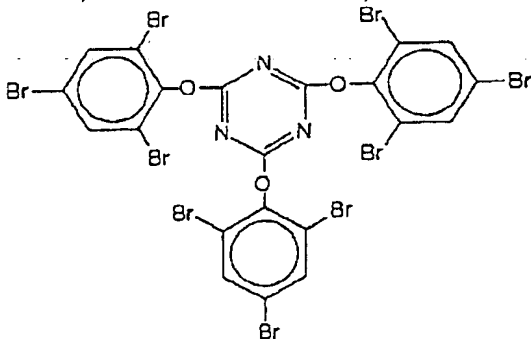
[0053] It is a bromination bisphenol system flame retarder (PURASEFUTI EB-242, the MANAC, INC. make, structure expression) in the example 7 toluene 80 weight section. [Formula 5]



20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0054] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 8 example 7. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 5×10^{16} ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was evaluated, in UL-94 specification, it was V-0.

[0055] It is a bromination aromatic series triazine system flame retarder (the Dai-Ichi Kogyo Seiyaku Co., Ltd. make, PIROGADO SR 245, structure expression) in the example 9 toluene 80 weight section. [Formula 6]

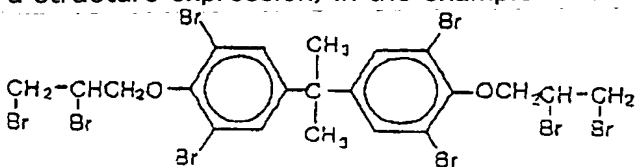


20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0056] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 10 example 9. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 3×10^{16} ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was

evaluated, in UL-94 specification, it was V-0.

[0057] It is a bisphenol system flame retarder (the fire guard 3100, Teijin formation incorporated company make, a structure expression) in the example 11 toluene 80 weight section. [Formula 7]



20 weight sections dissolution was carried out. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, precipitation, separation, etc. were not produced but it became a uniform solution.

[0058] The laminate was obtained by the same approach as an example 3 using the cross-linking norbornene system resin constituent solution obtained in the example 12 example 11. Even if this laminate contacted the 260-degree C pewter for 30 seconds, the above, such as exfoliation of copper foil and blistering, was not accepted, but water absorption was [the dielectric constant in 3x10¹⁶ ohms and 1MHz and the dielectric dissipation factor of insulation resistance] 3.0 and 0.001 0.02%, respectively. The dissolution was not accepted, even if it was immersed in toluene and left this laminate for 24 hours. Moreover, when fire retardancy was evaluated, in UL-94 specification, it was V-2.

[0059] The liquefied epoxy system thermosetting constituent (what added the benzyl dimethylamine 0.2 weight section as curing agent in the Epicoat 5046 100 weight section by oil-ized shell company as hardening mold epoxy system compound as dicyandiamide 4 weight section, dimethylformamide 14 weight section, and hardening assistant) 70 weight section of example of comparison 1 hyperviscosity was distributed and dissolved into the methyl-ethyl-ketone 100 weight section.

[0060] The glass-fabrics base material with a thickness of 0.1mm was immersed in this solution. After drying the glass-fabrics base material into which this epoxy system thermosetting constituent was infiltrated at 60 degrees C for 10 minutes, it was left for 10 minutes at 150 degrees C, and eight prepregs were obtained. About 50% of the weight of this prepreg was a cross-linking norbornene system resin constituent, and thickness was about 130 micrometers.

[0061] The laminating of this prepreg of eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for about 90 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press pressure 40 kgf/cm² might make 1mm in thickness.

[0062] Although abnormalities, such as exfoliation of copper foil and blistering, were not accepted even if this laminate contacted the 260-degree C pewter for 30 seconds, 0.15%, water absorption was 4.8 and 0.022 and the insulation resistance of absorptivity, a dielectric constant, and a dielectric dissipation factor was not respectively, desirable [water absorption / the dielectric constant in 1x10¹⁵ ohms and 1MHz and the dielectric dissipation factor] as an electrical insulation material.

[0063] When the example of comparison 2 hydrogenation ring breakage norbornene system resin (ZEONEX 280) 20 weight section and the dicumyl peroxide 1 weight section were distributed in the toluene 80 weight section, precipitation etc. was not produced but it became a uniform solution.

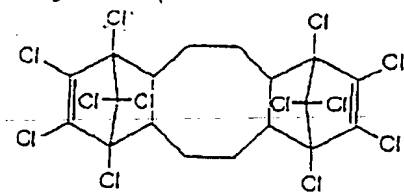
[0064] It applied so that it might become 750 micrometers in thickness on the SUS plate which made the mirror plane to this cross-linking norbornene system resin constituent solution using the coater. Leave it at 120 more degrees C for 10 minutes for 20 minutes, and it was made to dry at 60 degrees C, and removed from the SUS plate after that. The thickness of the obtained sheet was about 150 micrometers.

[0065] The laminating of these eight sheets was carried out, the laminating of the 35-micrometer copper foil was further carried out to both sides, it pressed for 20 minutes, and heat welding was carried out and the laminate was obtained so that the press temperature of 180 degrees C and press ** 40 kgf/cm² might make 1mm in thickness.

[0066] When this laminate contacted the 260-degree C pewter for 30 seconds, exfoliation of copper foil and generating of blistering were accepted and deformation was accepted further.

[0067] When it was immersed in toluene and this laminate was left for 24 hours, most laminates dissolved.

[0068] It is an annular chloroparaffin system flame retarder (a DEKURO lamp lath, oxy-dental chemical incorporated company make, structure expression) to the example of comparison 3 toluene 80 weight section. [Formula 8]



20 weight sections were dissolved. When it mixed with the resin solution 100 weight section which obtained this solution 100 weight section in the example 1, it did not dissolve, but precipitation was produced when it was left for one week.

[0069]

[Effect of the Invention] Even if it contacts a 260-degree C pewter for 30 seconds, neither exfoliation of copper foil nor generating of blistering takes place, but it is [the mold goods which constructed the bridge in the cross-linking norbornene system resin constituent of this invention are excellent in thermal resistance, chemical resistance, moisture resistance, the water resisting property, and the electrical property, and / be / it / hard coming to dissolve in toluene] excellent [mold goods] in especially thermal resistance and chemical resistance, and they do not have nonuniformity, and are useful as the RF circuit board etc.

[Translation done.]

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.